Pyrochemical separation of spent nuclear fuel: advances in the frame of the European ACSEPT project

"Actinide reCycling by SEParation and Transmutation"

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www.acsept.org

2012 International Pyroprocessing Research Conference
August, 26-29 2012
The Abbey Resort, Fontana, WI

ACSEPT program

PYROREP 2000-2003	→	EUROPART 2004-2007	→	ACSEPT 2008-2012

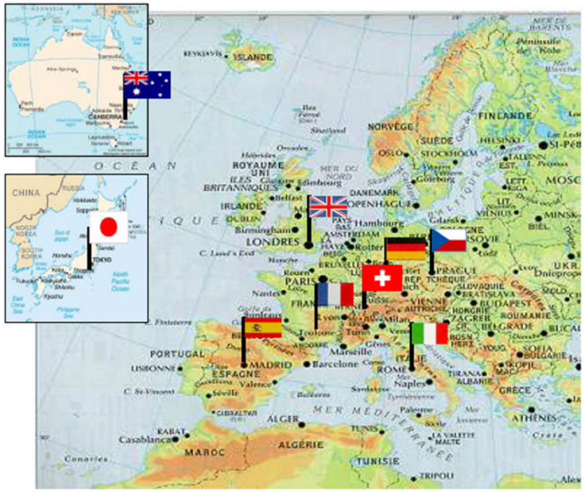
- 4.5 years R&D program, from March 2008 to September 2012
- Funded by the EC within the 7th framework program
- 12 European countries (+Australia and Japan) – 34 partners

Objectives: develop chemical separation processes (hydro+pyro) compatible with fuel fabrication techniques, in view of their future demonstration at the pilot level

S. Bourg, C. Hill, C. Caravaca, C. Rhodes, C. Ekberg, R. Taylor, A. Geiste, G. Modolo, L. Cassayre, R. Malmbeck, M. Harrison, G. de Angelis, A. Espartero, S. Bouvet, N. Ouvrier, Nuclear Engineering and Design (2011)

Pyrochemistry within ACSEPT

Activities in pyrochemistry: 15 partners, 9 countries



ANSTO, Australia
EDF, France
CEA, France
CIEMAT, Spain
CNRS, France
CRIEPI, Japan
ENEA, Italy
JRC-ITU, Germany
NLL, UK
NRI, Czech Republic
PoliMi, Italy
PSI, Switzerland
Rio Tinto Alcan, France
UPMC, France
UEDIN, UK

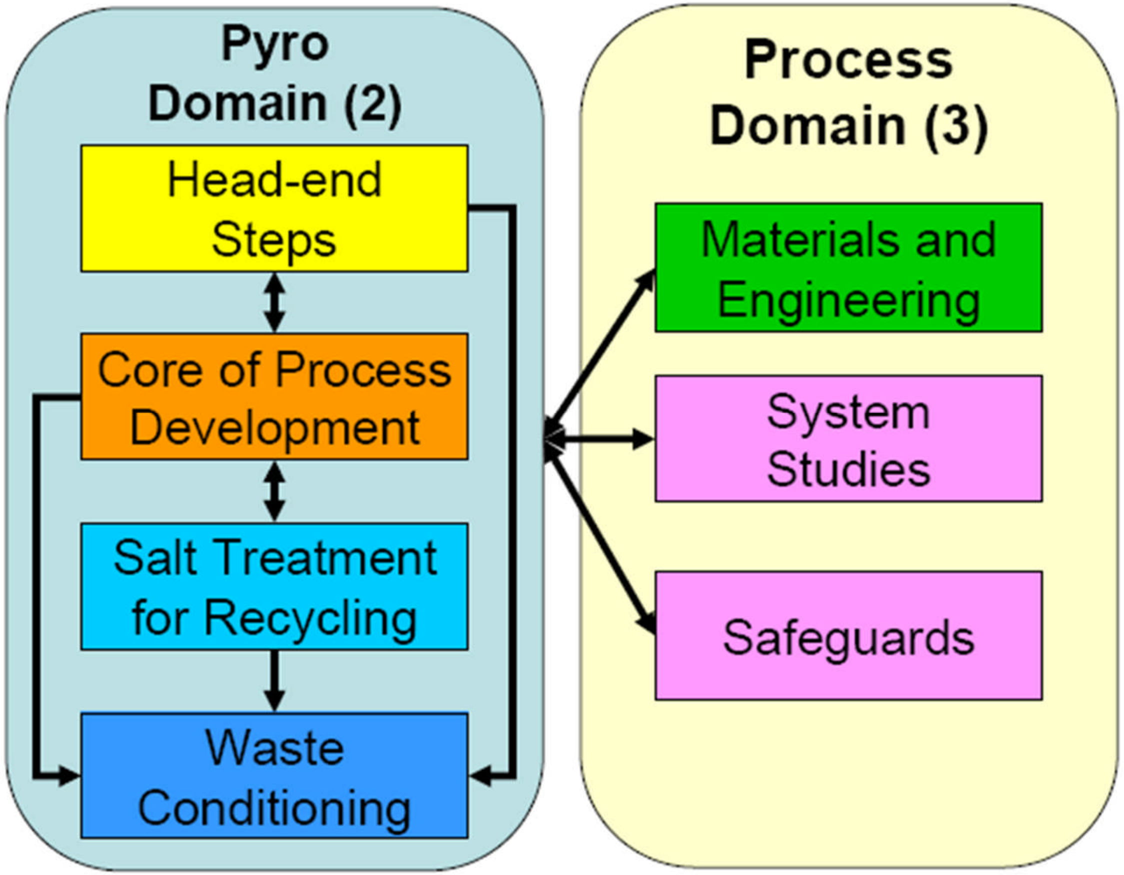
2008: Presentation of the ACSEPT program at the 2008 IPRC meeting (Korea)

2010: ACSEPT International Meeting, Lisbon, Portugal

2011: ACSEPT-Korea-Russia exchange meeting, Manchester, UK

2011: ACSEPT-ANL exchange meeting, Goteborg, Sweden

Pyrochemistry within ACSEPT

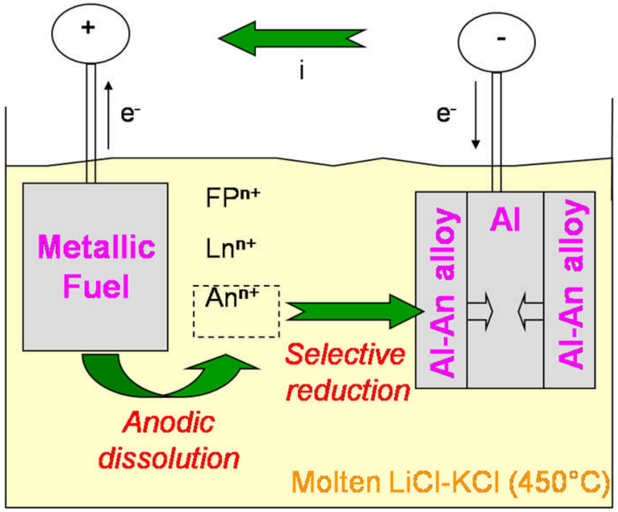


Core of Process

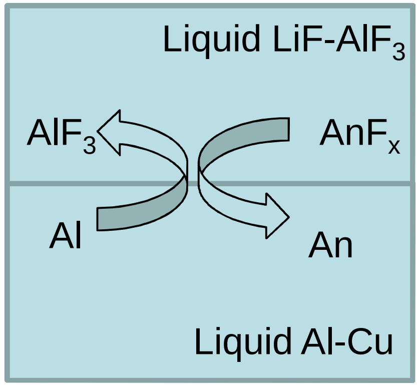
PYROREP+EUROPART = Identification of two reference separation processes: grouped extraction of An dissolved in molten salt by alloying with aluminium

➢ Electrorefining of actinides onto solid aluminium cathode in molten chloride salts (T~450°C)

P. Soucek, R. Malmbeck, C. Nourry, J.-P. Glatz, Energy Procedia (2011)



Principle of the electrorefining



Principle of the liquid-liquid extraction

➢ Liquid-liquid reductive extraction in molten fluoride salts/liquid aluminium (T~830°C)

J. Lacquement, H. Boussier, A. Laplace, O. Conocar, A. Grandjean, Journal of Fluorine Chemistry (2009)

Core of Process

Activities within ACSEPT

- Electrochemical processes in molten chloride salts
  - maximization of An recovery (exhaustive electrolysis) (ITU,CEA,RTA, CNRS)
  - An-Al alloying properties (ITU,CIEMAT,CEA)

Np-Al: P. Soucek, R. Malmbeck, E. Mendes, C. Nourry, D. Sedmidubsky, J.-P. Glatz, Journal of Nuclear Materials (2009)
Am-Al: G. De Cordoba, A. Laplace, O. Conocar, J. Lacquement, Journal of Nuclear Materials (2009)
Pu-Al: E. Mendes, R. Malmbeck, C. Nourry, P. Soucek, J.-P. Glatz, Journal of Nuclear Materials (2012)

- Electrochemical processes in molten fluoride salts

  Investigation of novel separation processes by electrochemical methods (ITU, ANSTO, NRI, CNRS, CEA)

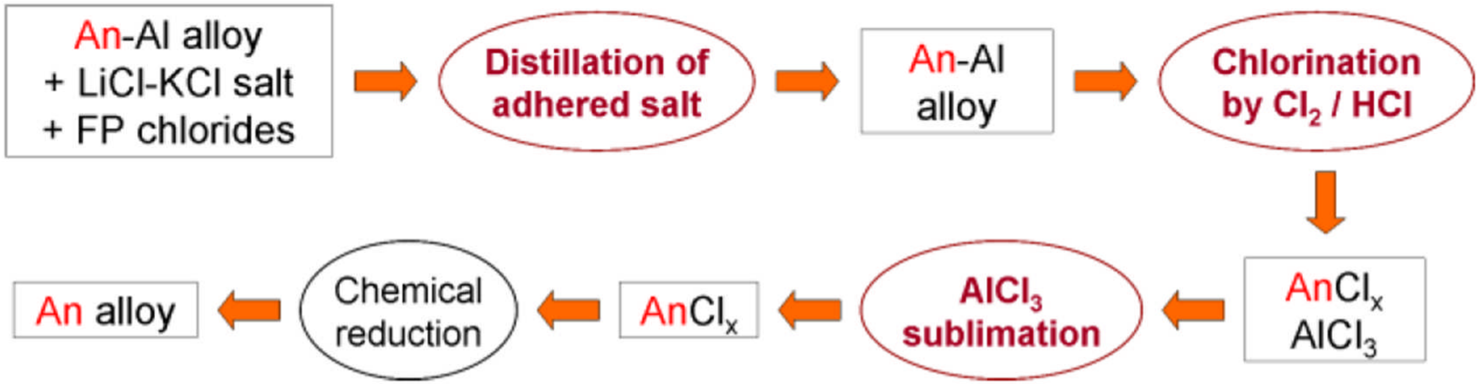
U: C. Nourry, P. Souček, L. Massot, R. Malmbeck, P. Chamelot, J.-P. Glatz, Journal of Nuclear Materials (2012)
N_2: L. Massot, P. Chamelot, M. Gibilaro, L. Cassayre, P. Taxil, Electrochimica Acta (2011)
La: C.P. Fabian, V. Luca, P. Chamelot, L. Massot, C. Caravaca, G.R. Lumpkin, Journal of the Electrochemical Society (2012)

- Methods for the recovery of An from Al

  Investigation of chemical (chlorination, hydrochlorination) and electrochemical routes, in order to maximize An recovery and recycle Al (CEA, ITU)

Core of Process

Chlorination for An recovery from An-Al alloys



Chlorination route for An recovery

Exp. step	*Temp.*	*Time*	*Conditions*
Distillation	800°C	8 hrs	Vacuum, $4\text{-}6{\cdot}10^{-2}$ mbar
Chlorination	150°C	2 × 20 hrs	Cl_2, molar ratio Cl_2/alloy = 36
Sublimation	400°C	5 hrs	Ar

Chlorination runs on U-Al and U-Pu-Al

- Optimal T=150°C (no UCl_5/UCl_6 losses)
- But slow kinetics
- Hydrochlorination at 450°C is more efficient

L. Cassayre, P. Soucek, E. Mendes, R. Malmbeck, C. Nourry, R. Eloirdi, J.-P. Glatz, Journal of Nuclear Materials (2011)

Core of Process

Exhaustive electrolysis (//An drawdawn)

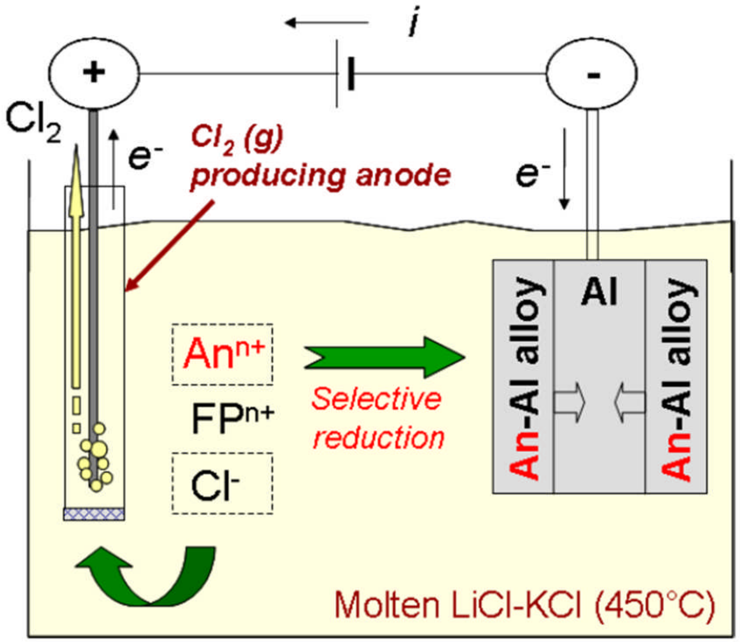
Objectives

FP removal from the electrorefining salt

=> Requires An removal in a first step

Principle

- An selective recovery on Al cathode
- Cl_2(g) evolving anode



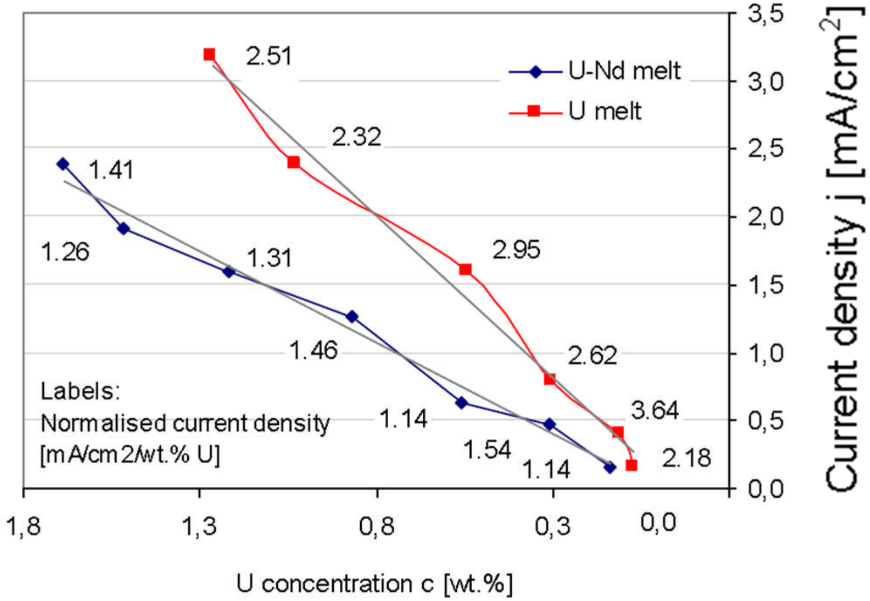
Principle of the exhaustive electrolysis

P. Soucek; R. Malmbeck, E. Mendes, C. Nourry, J.-P. Glatz , Journal of Radioanalytical and Nuclear Chemistry (2010)

Core of Process

Exhaustive electrolysis

Experimental tests on:
- LiCl-KCl-2.2wt%UCl_3
- LiCl-KCl-1.7wt%UCl_3-1.7wt%$NdCl_3$

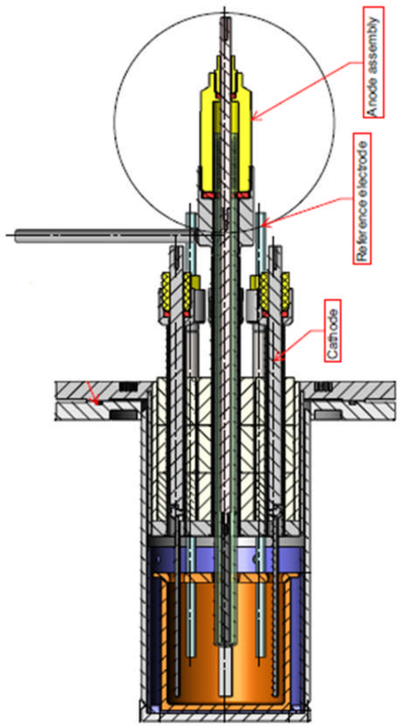


Maximal applicable current densities vs. U concentration

⇒ Efficient salt cleaning achieved (U down to 0.07 and 0.14wt%) without Nd codeposition
BUT

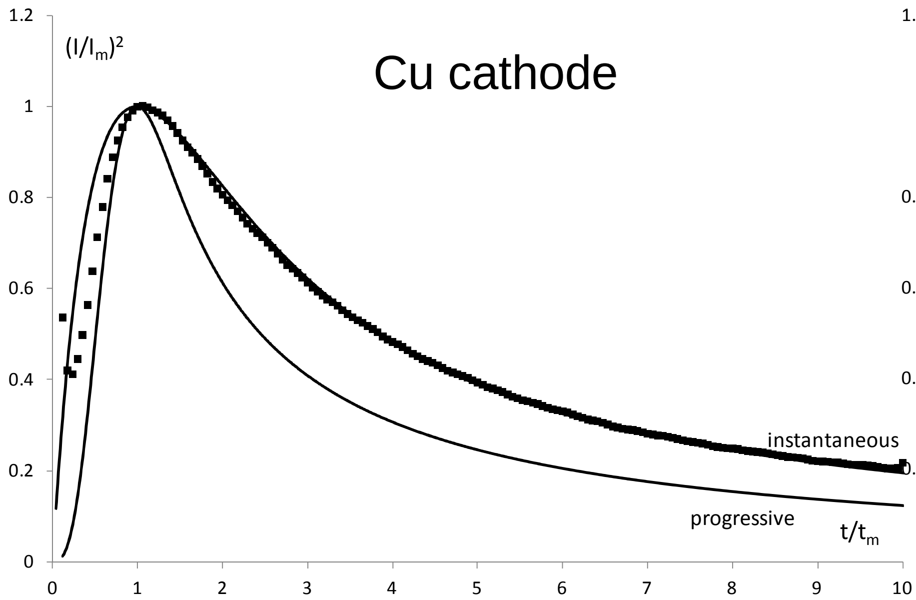
- Low current density ~2mA.cm^{-2}.wt%$(U)^{-1}$
- Long electrolysis time
- Corrosion of metallic elements by Cl_2(g)

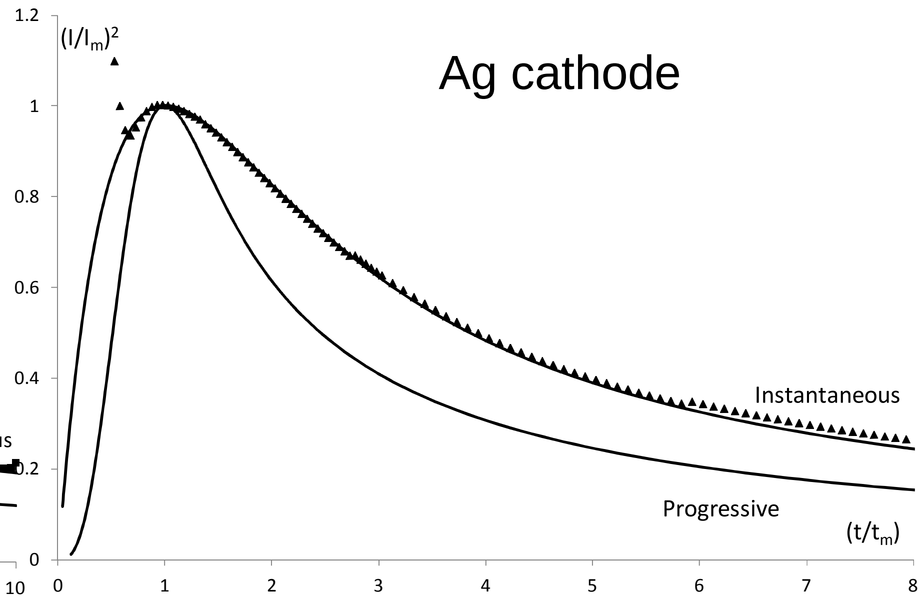
⇒ Design of a new electrorefiner



Core of Process

U nucleation model in LiF-CaF$_2$-UF$_3$ melts





LiF-CaF$_2$-UF$_3$ (3.3 10^{-2} mol/kg) on Cu at 840°C,
E =-1.27 V/ref. Pt , quasi reference : Pt.

LiF-CaF$_2$-UF$_3$ (3.3 10^{-2} mol/kg) on Ag at 840°C,
E =-1.30 V/ref. Pt , quasi reference : Pt.

=> Instantaneous nucleation

all the nuclei are created at the same time at the beginning of electrolysis

Head-end Steps

Objectives

- Removal of volatile FP
- Fuel conversion for dissolution/electrodissolution in salts suitable with the core of process

Activities within ACSEPT

- Thermal treatment (PSI)
- Chemical conversion (hydrofluorination) (CEA)
- Electrochemical conversion

- Direct reduction in chloride salts (Ln oxides) (CIEMAT)
- Direct reduction in fluoride salts (MeO_2 and UO_2) (CNRS)

Provides metal phase suitable for anodic electrodissolution

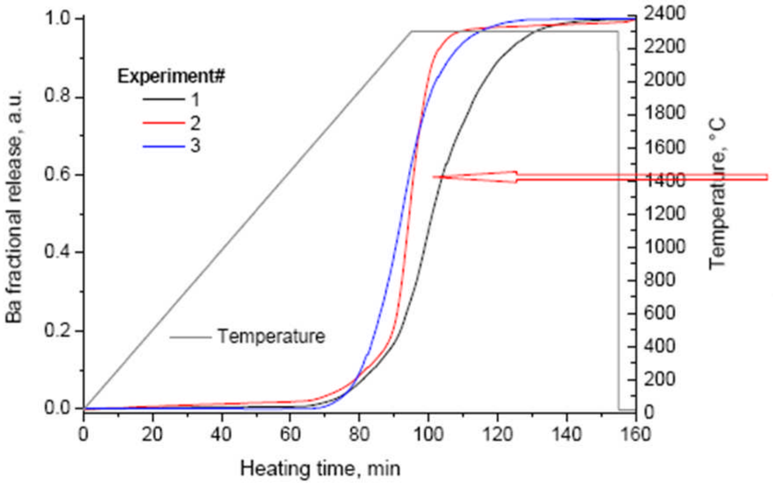
- Direct electrodissolution of oxide fuel in fluoride salts (MeO_2 and UO_2) (CNRS)

Head-end Steps

Thermal treatment

Objectives

• Study the release of FPs during the high temperature treatment of SIMFUEL and irradiated fuel
• Modeling the FP release (kinetics and thermodynamics) to support experimental work



✓ Reproducible results for most of the FPs

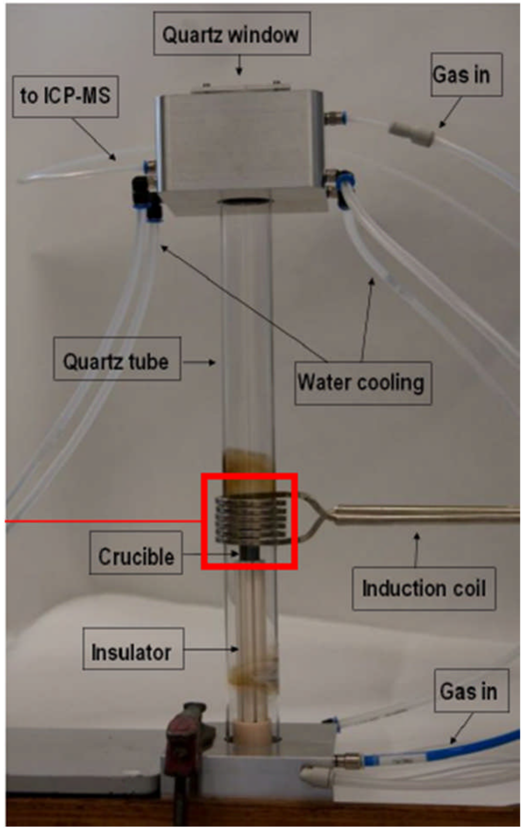
✓Output data format - transient signals of FPs by ICP-MS

Kinetics of the FP release

✓ No internal standard

Semi-quantitative analysis

PAUL SCHERRER INSTITUT

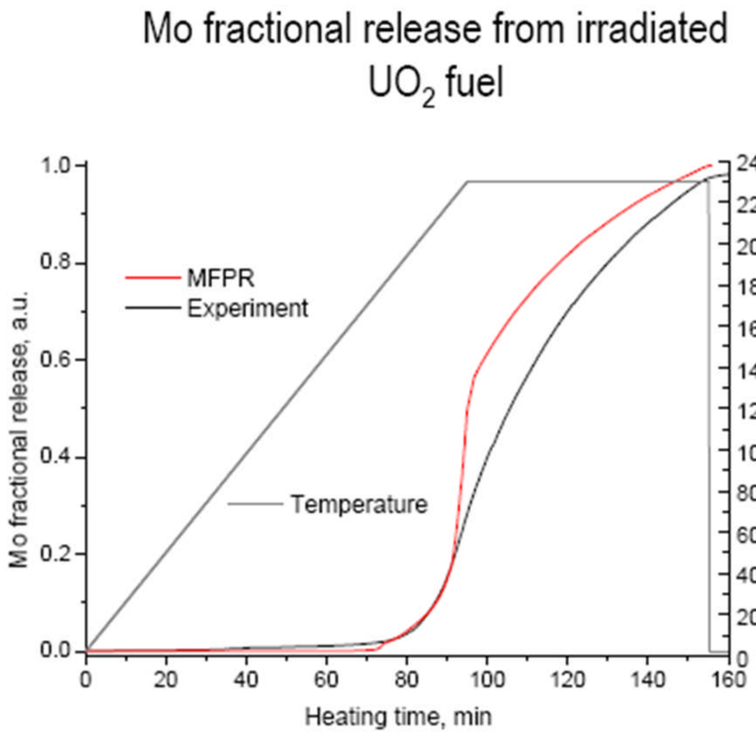


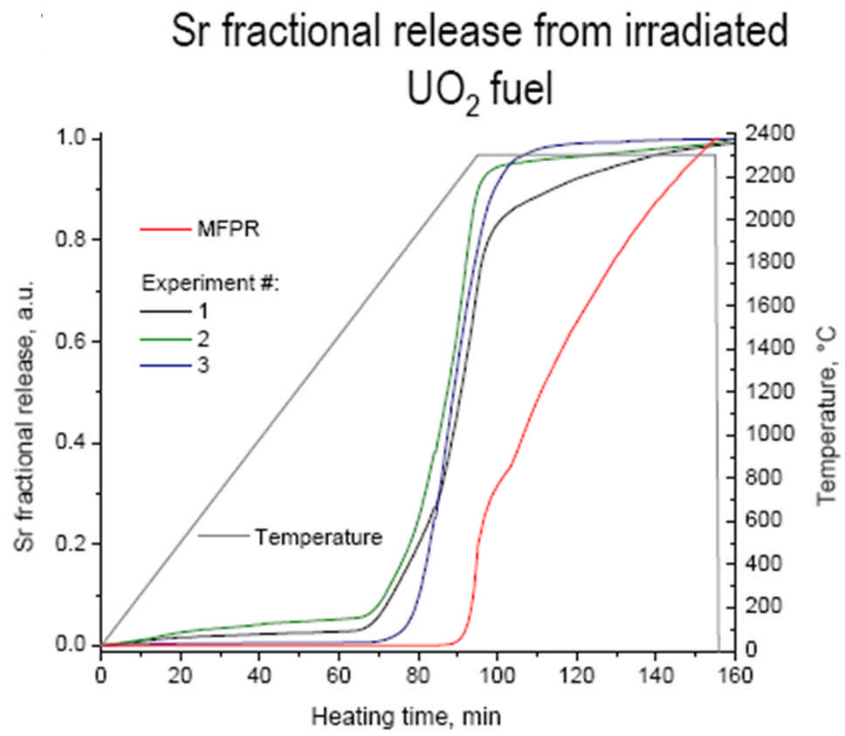
High temperature inductive heating device (InVap)

I. Günther-Leopold, N. Kivel, N. Shcherbina, European Winterconference on Plasma Spectrochemistry (2011)

Head-end Steps

Thermal treatment: modeling vs. experiments





Excellent agreement for some FPs (Xe, Cs, Ba, Mo, Zr)
Modeling to be improved for others (I, Sr)

Head-end Steps

Fuel conversion: direct reduction of UO_2 in $LiF-CaF_2$

No initial experience in direct reduction

=> Several oxides were tested according to expected increasing difficulty (electronic conductivity, Gibbs energy of formation)

SnO_2: good electronic conductor, Sn liquid at low T

Fe_3O_4: good electronic conductor

TiO, TiO_2: poor conductors, widely studied in chloride melts

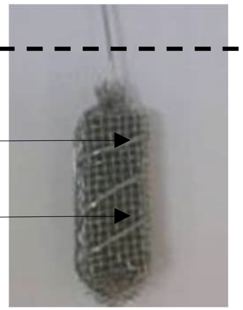
UO_2: poor conductor, radioactive material

$\Delta_f G° << 0$

Anode: Gold spiral

Cathode: oxide in Mo mesh

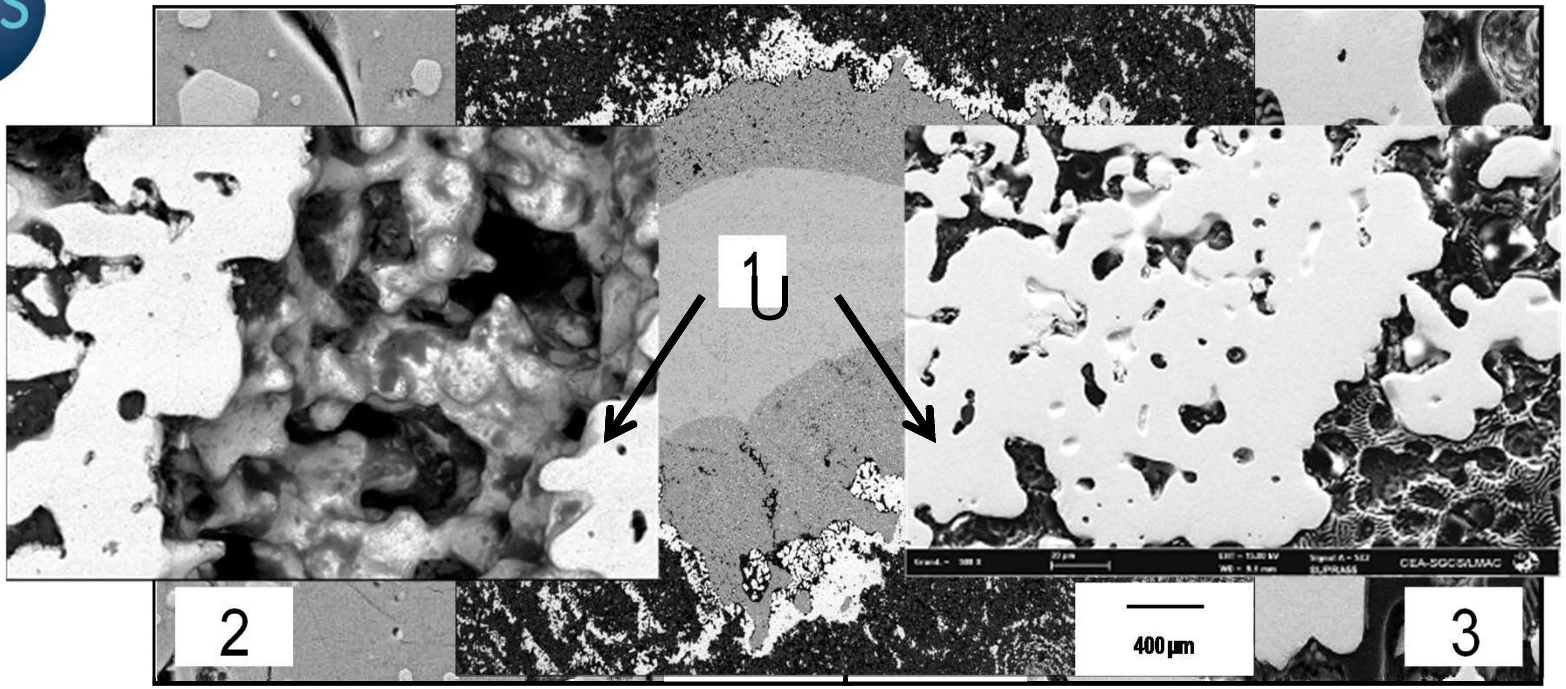
Salt: $LiF-CaF_2$ eutectic



M. Gibilaro, J. Pivato, L. Cassayre, L. Massot, P. Chamelot, P. Taxil, Electrochimica Acta (2011)

Head-end Steps

Fuel conversion: direct reduction of UO_2 in LiF-CaF_2



Micrographs of cross section of reduced samples: I=-0,15A//-0.30A for t=8000s

- Initial stage of reduction observed at the grain boundary in the partially reduced region with uranium metallic grains
- Full reduction achieved, typical coral-like structure

M. Gibilaro, L. Cassayre, O. Lemoine, L. Massot, O. Dugne, R. Malmbeck, P. Chamelot, Journal of Nuclear Material (2011)

Salt Treatment

Objective

Treatment of the salts used in the core of process (loaded with Ln and other FP) - minimize wastes ; re-use of the salt

Activities within ACSEPT

- Development of a decontamination process for chloride salts
  - Development of a Zeolite column for FP removal (UK-NNL)
  - Water vapor/Argon sparge precipitation (CEA, CNRS)
  - Test of a liquid lead cathode for removal of Cs, Sr, Ba and Rb (CIEMAT)
  - Development of an aqueous ion-exchange process (ANSTO)
  - Investigation of distillation as technique for decontamination of $LiF-AlF_3$ from liquid-liquid reductive extraction process (CEA)

- Studies of FP behaviour in molten chloride and fluoride salts
  - Speciation (NMR) of La and Cs in oxide containing molten fluorides (CNRS)
  - Development of Molecular Dynamics models in molten salts (UPMC), for salt properties (density, viscosity, conductivity) determination

C. Bessada, O. Pauvert, D. Zanghi, A.-L. Rollet, V. Sarou-Kanian, M. Gobet, G. Moussaed, A. Rakhmatullin, M. Salanne, C. Simon, ECS Transactions (2010)

Salt Treatment

Zeolite ion-exchange

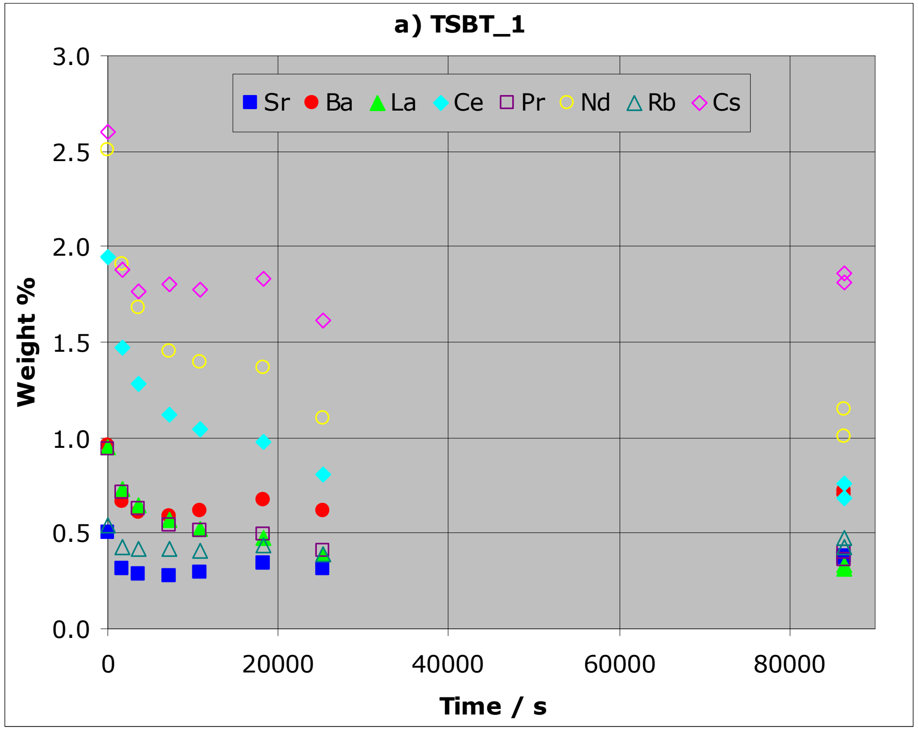
National Nuclear Laboratory

- Reliable decontamination factors determined for range of fission products
Agree with expectations, i.e. RE > AE

Element	Nd^{3+}	Ce^{3+}	Sm^{3+}	Eu^{3+}	Eu^{2+}	Sr^{2+}	Ba^{2}
DF	10.0	8.0	6.7	2.5	2.9	2.2	1.8

- Reference Waste Salt experiments:
Competition effects between +3 (Ln) and +2 species (Sr, Ba)
Alkali metals (Cs, Rb) rapidly reach a constant concentration, whereas the La, Ce, Pr and Nd all continue to ion-exchange over the full 24 hours of the experiment.

The degree of ion-exchange depends on the starting concentrations of all the species present.



EURATOM

Salt Treatment

Comparison of processes

National Nuclear Laboratory

Salt Decontamination Process	Lanthanides (La, Ce, Nd, Pr)	Alkaline Earths (Sr, Ba)	Alkali Metals (Cs, Rb)
Ion-exchange (zeolites)			
Hybrid aqueous closed loop			
Precipitation (carbonates/phosphates)			
Precipitation (oxygen sparging)			
Precipitation (wet argon sparging)			
Electrolysis			
Li-Reduction			
Melt crystallisation			

Fully effective, demonstrated at lab-scale (>90% efficient)
Partially effective, demonstrated at lab-scale (10-90% efficient)
Slightly effective, demonstrated at lab-scale (<10% efficient)
Ineffective, demonstrated at lab-scale (0% efficient)
Assumed effective, but not fully demonstrated

Salt Decontamination Process	Advantages	Disadvantages
Ion-exchange (zeolites)	Removes all FPs.	Low DFs for AMs and AEs High waste volume.
Hybrid aqueous closed loop	Removes all FPs. Wasteform contains no chloride.	Limited experimental data. Not fully demonstrated. Complex flowsheet. Re-conditioning of salt required.
Precipitation (wet argon sparging)	Effective for Ln's.	Not fully demonstrated. Combination of water and melted salt.
Electrolysis	Effective for Ln's	Ineffective for AMs & AEs. Evolution of chlorine.

Waste Conditioning

Objectives

Conditioning of chloride, fluoride and metallic wastes arising from pyro processes

Activities within ACSEPT

- Assessment of sodalite as candidate matrix for spent chloride salt confinement
  - Synthesis of Li-K sodalite (100 g scale) (ENEA)
  - Validation of pure Li-K sodalite as a potential matrix (CEA, PoliMi)

- Chloroapatite as an alternative matrix for spent chloride salt confinement
  - Synthesis of a chloroapatite phase for the incorporation of alkaline, alkaline earth and rare earth elements (CEA)

- Confinement of metallic fission products
  - Immobilization of noble FP (Pd, Mo, Tu, Rh) by formation of metallic solid solutions (Cu-Ni, Cu-Sn, Al)(CEA)

Waste Conditioning

Ceramic processing

- **Sodalite based ($Na_8Al_6Si_6O_{24}Cl_2$) ceramic** processing with Hot Uniaxial Press (HUP) or Pressureless Consolidation (PC)

G. De Angelis presentation

- **Chloroapatite $Ca_{10}(PO_4)_6Cl_2$**

$3\ Ca_3(PO_4)_2 + CaCl_2 \rightarrow Ca_{10}(PO_4)_6Cl_2$: calcination at 850°C/3x12h

- **Chlorospodiosite Ca_2PO_4Cl**

$Ca_3(PO_4)_2 + CaCl_2 \rightarrow 2\ Ca_2(PO_4)Cl$: calcination at 750°C/3x15h

- Sintering by HUP
- Process optimisation (T, P, duration): densification ratios > 92%

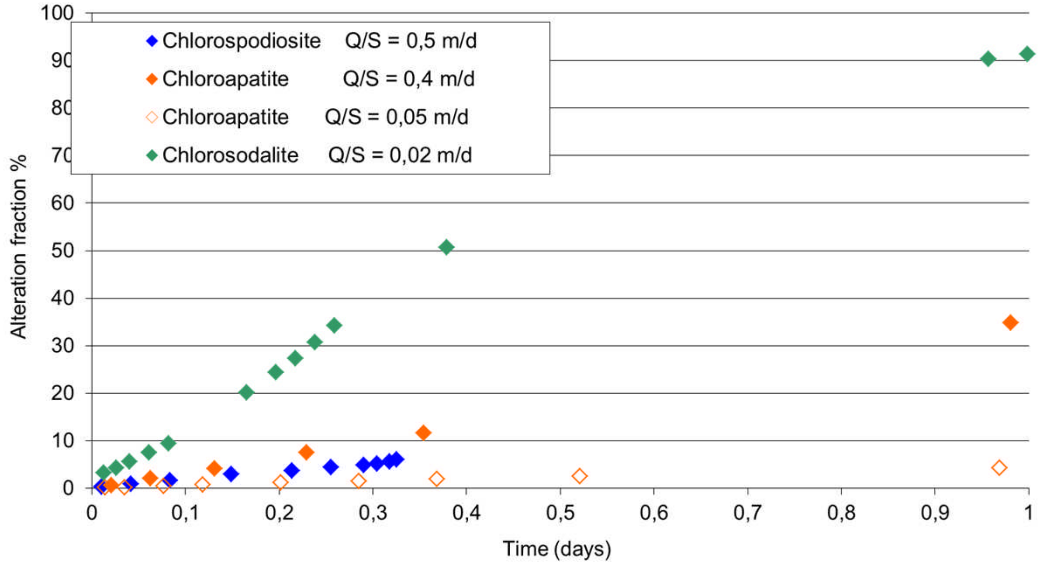
Waste Conditioning

Leaching tests

- Static leaching tests:
  - Contact time (1-7-15-30-90-150 days)
  - Temperature (25°C and 90°C)
- Dynamic Soxhlet tests at 100°C for 0.3-1-3-7-10 days

Sodalite phase: significant release of chloride salt, high initial dissolution rate at 100°C in pure water, and holes in the matrix after 150 days leaching at 90°C.
⇒sodalite phase cannot be retained as a suitable matrix

Better behaviour of chloroapatite – to be confirmed with long term tests



Comparison of the alteration fraction (NL x Sspec, %) of chloroapatite, chlorospodiosite and chlorosodalite versus time

Concluding remarks

➢ ACSEPT final meeting will take place at the end of the Atalante meeting (Montpellier, France)

➢ Following Fukushima accident, EC policy regarding nuclear fission research programs has changed: new programs focused on safety of existing reactors, no new developments (e.g. GENIV) except for An burning (double strata concept)

➢ However, the SACSESS (Safety of ACtinide SEparation proceSSes) program will be funded by EC, starting in 2013

- Pyro activities will be focused on treatment of ADS matrices (cercer and cermet), online monitoring and basic data acquisition

Thank you for your attention!